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# An Interpenetrating Polymer Network for Second-Order Nonlinear Optics

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The linear optical and second-order nonlinear optical (NLO) properties of an interpenetrating polymer network (IPN) have been investigated. For the poled and cured IPN samples, large second-order NLO coefficients,  $d_{33}$ , were measured at 1.064  $\mu\text{m}$  and 1.542  $\mu\text{m}$ . The linear electro-optic coefficients,  $r_{33}$ , were determined at various wavelengths. The poled and cured IPN samples showed no measurable decay of the second-order optical nonlinearity after being treated at 110 °C for more than 1000 hours. This excellent long-term stability of the NLO property is ascribed to the novel interpenetrating crosslinked molecular structure of the IPN system.

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## 1. Introduction

Second-order nonlinear optical (NLO) polymeric materials have recently attracted a great deal of interest because of their potential applications in integrated optical devices, such as waveguide electro-optic modulators, switches and optical frequency doubling devices [1-7]. The interest in these polymeric materials is mainly due to their large optical nonlinearities, low dielectric constants and ease of waveguide processability. In order to be used in practical devices, the poled polymers must possess large second-order optical nonlinearities which should be sufficiently stable at ambient temperature for a long period of time. Many approaches to improve the temporal stability have been reported by a number of research groups [8-24]. Crosslinking reactions have been extensively employed to enhance stability of second-order NLO properties in several poled polymer systems [8,11,15-21]. The resulting crosslinked networks usually possess high glass transition temperatures ( $T_g$ ) and dense matrices which reduce the mobility of the polymer chains. These features prevent the aligned NLO chromophores from relaxing to a random orientation. However, slow decay of second-order NLO properties at elevated temperatures was still observed in the poled polymers.

Recently, we have taken a novel approach to achieve stable second-order NLO polymers by incorporating NLO moieties into an interpenetrating polymer network (IPN) [25]. This IPN combines a network of an NLO active epoxy-based polymer [20] and a network of an NLO active phenoxy-silicon polymer [21]. The NLO epoxy-based network is prepared from an epoxy prepolymer (BPAZO, fig. 1 (a)) based on the diglycidyl ether of bisphenol A and 4(4'-nitrophenylazo)aniline (Disperse Orange 3, DO3) functionalized with crosslinkable acryloyl groups [20]. The NLO phenoxy-silicon polymer is based on an alkoxysilane dye (ASD, fig. 1 (b)) of (3-glycidoxypropyl)trimethoxysilane

and DO3, and the multifunctional phenoxy molecule 1,1,1-tris(4-hydroxyphenyl)ethane (THPE, fig. 1 (c)). Each network is formed simultaneously at 200 °C in a noninterfering manner. The epoxy prepolymer forms a network through acryloyl groups which are reactive at high temperatures without the aid of any catalyst or initiator. The phenoxy-silicon polymer network is formed by a sol-gel process which consists of sequential hydrolysis and condensation reactions. For this IPN system, an excellent temporal stability of the second-order optical nonlinearity was achieved. In this paper, we report on the optical characterizations on this IPN based material. The linear optical and second-order NLO properties of the IPN system are presented. Excellent long-term stability of the second-order optical nonlinearity at 110 °C in this material has been obtained.

**Insert fig. 1.**

## **2. Experimental Details**

To prepare good optical quality thin films by spin-coating, ASD and THPE with molar ratio of 1.0 : 1.17 were co-dissolved in a mixed solvent (propylene glycol methyl ether acetate : 1,4-dioxane = 3 : 1(v/v)) with a small amount of water and base catalyst [25]. BPAZO, which was dissolved in the same solvent was subsequently added into this solution. The resulting solution contains a weight ratio of 1 to 1 for BPAZO to ASD/THPE. The solution was then spin-coated onto glass microscope slides. The resulting thin films exhibit good optical quality. The corona poling technique [3,8,20,21] was employed to align the NLO chromophores. The corona field was applied as the temperature was raised to 80 °C. The temperature was then increased slowly to 200 °C with the corona field on. The corona current was maintained at 2  $\mu$ A with a potential of 4 kV while

the poling temperature was kept at 200 °C for 60 minutes. The formation of the polymer networks and the molecular alignment for the poled order proceeded simultaneously during this period. The 60 minutes poling/curing time was chosen to allow the polymers to have sufficient time for crosslinking. The samples were then cooled down slowly to room temperature before the corona field was discontinued. The typical thickness of the cured films was approximately 0.6  $\mu\text{m}$ . The poled and cured IPN samples also show good optical quality.

UV/Vis spectra of the IPN samples were recorded with a spectrophotometer. An ellipsometer was used to measure the refractive index of the samples. The linear electro-optic coefficients of the poled IPN samples at various laser wavelengths were determined using a reflection method [26]. The second-order NLO coefficients,  $d_{33}$ , of the poled IPN samples were characterized by the second harmonic generation (SHG) technique from 1.064  $\mu\text{m}$  laser radiation and the Raman shifted wavelength (from a high pressure methane cell) at 1.542  $\mu\text{m}$ . The details of the SHG measurement were discussed elsewhere [20,21]. The relaxation behavior of the second-order NLO properties was studied by monitoring the decay of the second harmonic intensity at 532 nm as a function of time at elevated temperatures after poling and curing. The optical loss of the slab waveguide fabricated from the IPN was also evaluated. A right angle prism coupler and an optical fiber bundle were used for the measurement.

### **3. Results and Discussion**

The UV-Vis absorption spectra of the IPN are shown in fig. 2. The pristine sample shows the absorption maximum of the DO3 at 458 nm. The absorption peak shifts to 436 nm and the absorbance reduces right after poling and curing. The reduction of the absorbance and the peak shifting confirm the alignment of the chromophores as a result of poling [15]. However, some degrees of

sublimation or degradation during the curing and poling process also lead to some reduction of the absorbance. After the same sample was heated at 110 °C for 168 hours, the height of the absorption peak remained practically unchanged. This behavior implies that the chromophores did not degrade or sublime during this period of thermal treatment.

### **Insert fig. 2.**

The refractive indices of the IPN samples at 532, 633, 671, 775, and 830 nm, and 1.000  $\mu\text{m}$  were measured. A single-oscillator Sellmeier equation [27] was used to fit the experimental data,

$$n^2 - 1 = \frac{A}{\lambda_0^{-2} - \lambda^{-2}} + B,$$

where A is proportional to the oscillator strength,  $\lambda_0$  is the wavelength of the oscillator, and B accounts for nondispersive contributions from all other oscillators at shorter wavelengths. The value of  $\lambda_0$  was set to the spectroscopically measured value at 436 nm. The corresponding Sellmeier coefficients were determined to be  $A=1.399 \times 10^{-6} \text{ nm}^{-2}$  and  $B=1.357$ . The dispersion of refractive indices of the IPN sample is shown in fig. 3. The optical loss of the slab waveguide at 1.064  $\mu\text{m}$  was too high to be quantitatively measured. At 1.3  $\mu\text{m}$ , the optical loss was determined to be 8 dB/cm. The high optical loss in the waveguide could be attributed to the scattering loss from the waveguide, as well as to the absorption tail of the NLO chromophores and the polymers. Our recent studies showed that through chemical modifications on the polymers the optical loss of the IPN can be reduced significantly [28].

### **Insert fig. 3.**

The NLO coefficients,  $d_{33}$ , of the poled IPN samples were measured to be 33 pm/V and 5.5 pm/V at 1.064  $\mu\text{m}$  and 1.542  $\mu\text{m}$  respectively. Due to the absorption of the IPN at 532 nm, the  $d_{33}$  value measured at 1.064  $\mu\text{m}$  is resonantly enhanced. The linear electro-optic coefficients,  $r_{33}$ , at various laser wavelengths were also measured. The  $r_{33}$  value at 1.3  $\mu\text{m}$  was determined to be 5.1 pm/V. The wavelength dependence of the electro-optic coefficients is shown in fig. 4. The temporal stability of second-order nonlinearity for the poled and cured IPN samples was studied under ambient conditions at 110 °C. No decay of the second-order NLO property (the effective second-order NLO coefficient,  $d_{\text{eff}}$ ) of the IPN samples was observed after the samples were kept at 110 °C over 1000 hours as shown in fig. 5. One IPN sample was placed on a hot stage at 160 °C for 15 hours, 50% retention of the  $d_{33}$  value was still measured. This stability of the NLO property for the IPN system is a result of the high  $T_g$  of the polymers and the presence of crosslinked networks. In addition, permanent entanglements between the two networks further constrain the motion of aligned chromophores. Therefore, the mobility of the NLO chromophores is dramatically decreased which promotes the synergistic stability of the poled order.

### **Insert figs. 4 and 5.**

## **4. Conclusions**

In conclusion, a second-order NLO material with superb stability based on an IPN has been demonstrated. The poled and cured IPN samples exhibit large  $d$  coefficients and linear electro-optic coefficients. These IPN samples show no

change in the second-order optical nonlinearity after being heated at 110 °C for more than 1000 hours. This excellent long-term stability is ascribed to the novel interpenetrating crosslinked molecular architecture of the IPN system.

## **5. Acknowledgments**

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## Captions:

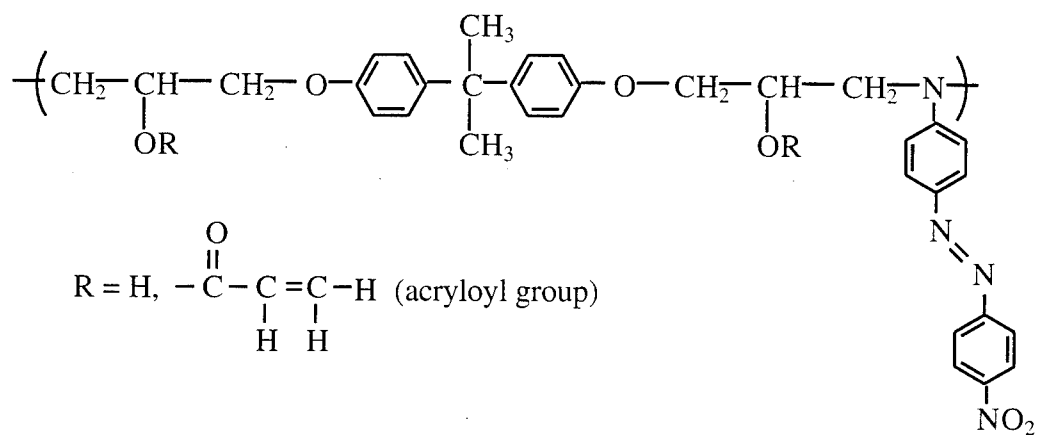
Fig. 1. Chemical structures of BPAZO, ASD and THPE.

Fig. 2. UV-Visible absorption spectra of the IPN sample: pristine, right after poling/curing, and poled/cured with thermal treatment at 110 °C for 168 hours.

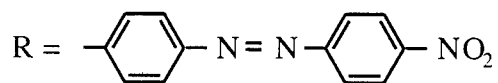
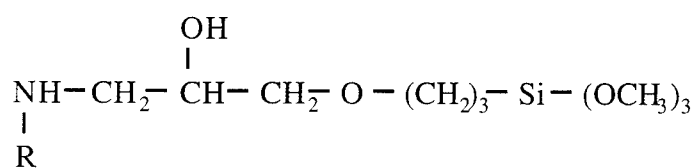
Fig. 3. Dispersion of the refractive index for the IPN.

Fig. 4. Electro-optic coefficient of the IPN as a function of wavelength.

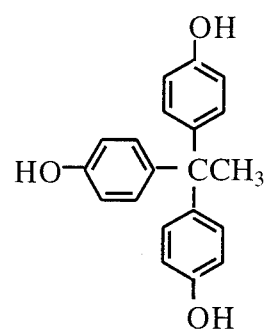
Fig. 5. Temporal behavior of the second-order NLO coefficient of the poled/cured IPN sample at 110 °C.



(a) BPAZO



(b) ASD



(c) THPE

